THESIS SUBMITTED FOR THE DEGREE

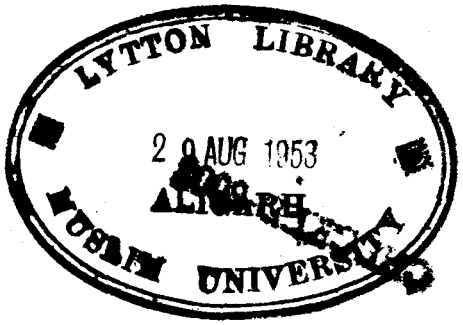
OF

MASTER OF SCIENCE

IN THE MUSLIM UNIVERSITY ALIGARH

BY

MOHD. IZHARUL HAQ FARUQI.



On the absorption spectra and linkage of Inorganic Nitrates in the vapour State

Thesis submitted for the degree of

Master of Science

in the Muslim University, Aligarh

by

Mohd Israrul Haq Faruqi.

I N T R O D U C T I O N [1]

Experiments of Franck and his collaborators [2] have shown that absorption spectra of diatomic salts in the vapour state are well qualified to distinguish between covalent and electrovalent linkage in such molecules *). Whereas alkali halides are electrovalent in the vapour state, as one would expect, halides of the first sub group of the periodic table, like those of silver, were found to possess a covalent bond and furnished for the first time a clear example, that a particular bond may change its character and be either covalent or electrovalent in the same molecule according to the experimental conditions. This result at the first moment surprising is naturally of great interest for any physical understanding of chemical linkage and made it desirable to extend such investigations to polyatomic molecules.

The criterion by which Franck was able to distinguish between atomic and ionic binding, was that the term of a molecule which originates in two neutral and unexcited atoms, naturally is the ground level of a covalent molecule but forms an excited term of an electrovalent one, because here the ground level is formed by a combination of two ions. This criterion cannot be used in the case of polyatomic molecules. Firstly it is known on account of the later investigations, that this criterion

---

*) A bond is termed 'covalent' here if the molecule dissociates into neutral atoms by adiabatic excitation of the vibrational levels of its ground state, and "electrovalent" if this adiabatic dissociation produces ions. We thus identify the chemical terminology with that of Franck (atomic molecules and ionic molecules), but it should be clearly understood, that we speak of the character of the bond of a molecule only under well defined experimental condition. It will be seen, that a bond, e.g. that between potassium

is not rigorously valid, partly because the combination of two atoms in particular states may give rise to a large number of attractive and repulsive terms, and partly because intersections of the potential curves of the electronic terms among themselves are quite possible. The results of absorption spectroscopy of polyatomic molecules is however, not surprising, since the number of repulsive terms increases rapidly with the number of constituent atoms and the excitation of an electron by illumination apparently means the transition from the ground-level of the molecule to an exited repulsive term, both together possessing the same level of unexcited atoms as the dissociation product. This is equivalent to an intersection of the two potential curves at large internuclear distance and may be taken as a special case of the second possibility, mentioned above. The dissociation of the ground level of a covalent molecule into excited atoms and of an excited molecular term into unexcited atoms owing to the intersection of two curves of the Franck-Condon diagram at small internuclear distance appears to be realised in a case like CsO. Photo-dissociation into unexcited

---

(CONTD. FROM PREVIOUS PAGE).

and oxygen in KNO_3, may be covalent in the vapour state and electrovalent in solution on account of the additional energy of hydration. Only with this proviso it is permissable to identify the chemical terminology with the above definition without confusion. A covalent bond may be polarised or not and the molecule possessing a dipolmoment or not will be termed a polar a non polar molecule respectively according to the terminology, introduced by Debye.

atoms obtains according to the continuous absorption spectrum [3], whereas the band spectrum indicates a covalent molecule in the vapour state and no perturbations have been found, warranting an explanation on the assumption of an hybridisation of the ionic and the atomic potential curve. It has been shown [4] that the ground level of such molecules does not arise from that of the two unexcited atoms but involves an excited metal atom in the state $sp\ ^3p$. The metal atom in its normal state s^2 the electron forming a closed group 1^2, gives rise to a repulsive curve which intersects that of the ground state of the molecule. Apparently this repulsive level which involves unexcited atoms forms the final state of the photo-lytic process. Experimentally the repulsive character of the s^2 configuration has been definitely confirmed by the band spectrum of CdF, where the discrepancy between the energies of excitation of the dissociation products and the energy differences between the excited terms and the ground state of Cd is too large to be explained by an inaccuracy of the Brige-Sponer method of linear extra-polation [5].

Besides these theoretical considerations also practical reasons do not permit the application of Franck's criterion to polyatomic salts. The fact, that the first photodissociation produces unexcited atoms in the alkali salts, was established by the agreement of the energy differences of the various regions of selective absorption with those of the atoms concerned. This procedure is not possible for polyatomic salts, because the electronic levels of the ions or radicals such as NO_3^- or the $-C-NO_2$ group are not known. I have therefore taken absorption spectra of some polyatomic inorganic salts

where it is possible to distinguish empirically between the spectrum of the covalent and the electrovalent form. Thus the spectrum of inorganic nitrates in solution is known along with that of HNO_3 and ethyl nitrate in the vapour state, that of potassium sulphate in solution along with dimethyl sulphate and diethyl sulphate in substance and in solution of other and that of the nitrite ion is known as well as that of ethyl nitrite in the vapour state. In all these cases the absorption spectrum of the covalent form, e.g. of the organic ester differs from that of the free ion in dilute aqueous solution and allows us to distinguish the electrovalent form from it. Details will be discussed below. Such compounds like nitrates appear to be suitable also because their decomposition on heating invariably liberates rather large quantities of NO_2, which can be recognised easily by its two characteristic sets of bands the first being at about 6000 to 3500 A.U., the second one from about 2400 A.U. onwards. It can be assumed, that the measured absorption spectra really correspond to that of the nondecomposed substance as long as these bands do not appear on the plates. The same bands served as an indicator of decomposition for the potassium nitrite and those of SO_2 at about 3000 A.U. and 2200 A.U. in the case of the sulphate. It will be seen that among the nitrates those of the alkali metals stand heating better than silver nitrate, and among the divalent nitrates $Cd(NO_3)_2$ decomposes very rapidly, $Pb(NO_3)_2$ and still more $Hg(NO_3)_2$ can be heated to higher temperatures. Again Ag_2SO_4 decomposes much more rapidly than K_2SO_4 and our impression according to these few experiments is, that decomposition on heating obtains the earlier the higher the ionisation potential of the metal atom or which is the same, the more the molecule becomes nonpolar

and the more it approaches the true homopolar type of binding on the other hand the stability of more complex molecules is naturally decreased very much and ammonium salts decompose at comparatively low temperatures. It was possible to study the absorption spectrum of ammonium nitrate but the decomposition of ammonium sulphate was so rapid and the amount of CO_2 liberated at low temperatures so great, that its spectrum could not be investigated.

Absorption Spectra of related substances and of salts in solution.

The absorption spectrum of the nitrate ion has been investigated by a number of authors and is very well known indeed, so much so that it is sometimes recommended for calibration purposes [6]. According to qualitative measurements of Hartley and K. Schaefer [7] the spectrum of nitric acid in diluted solutions in concentrations from 0.2 m to about 10 m exhibits a maximum in the region of 300 m u . Such a maximum is also characteristic for the nitrates of the alkali and earth alkali metals in solution. The maximum disappears gradually, with higher concentrations of the acid, up to 23.12 m (98.6 % acid), it flattens out more and more, until a continuous and absorption remains with a point of inflection in the region between 263 and about 273 m u. Scheafer and Hantzsch [8] ascribed the maximum of selective absorption at 300 m u in very diluted solutions to the nitrate ion, the end-absorption with the superimposed flat maximum at about 265 m u of the highly concentrated solutions to a covalent molecule $H - O - NO_2$.

Quantitative measurements of the absorption curve of nitrates and nitric acid in various solvents by v. Halban [9] and Scheibe [10] have confirmed this point of view. Mention may be made of the spectrum of nitric acid in hexane and of ethyl nitrate in the liquid state and insolution which show again a diffuse maximum at about 272 m u whereas the distinct maximum of inorgan nitrates in solutions of low concentrations lies at 302 m u. Finally the absorption curve of athyl nitrate in the vapour state was measured quantitatively by J.W.Goodeve [10], who obtain again a point of inflection between 278 and 244 m u. There is no doubt that these measurements establish a spectroscopical

criterion which enables us to distinguish between the true electrovalent and the true covalent bond in this particular case. The former one, i.e. the free nitrate ion exhibits a maximum of selective absorption at 302 m u, but whenever the linkage between the NO_3 group and the positive partner of the molecule is due to atomic binding and not to electrostatic forces between ions, this maximum disappears and is replaced by a very diffuse one, whose highest point is difficult to measure and sometimes not at all, but which lies approximately between 263 and 275 m u.

This interpretation of the spectrum in solutions of very low and very high concentrations is generally accepted, but that of solutions of nitrates and nitric acid of medium strength, up to about 10 m, is more difficult.

It is interesting to note, that the transition from covalent to electrovalent linkage depends to a very high degree on the nature of the solvent. For aqueous solutions the absorption curve of nitric acid shows an abundance of the electrovalent form up to a concentration of 9.22 m whereas in a concentration of 14.8 m a high percentage of covalent molecules is indicated. If an acid is used as solvent even in a diluted solution a great number of covalent molecules may be present, if the concentration of the acid, used as solvent is strong enough; thus in $HClO_4$ a concentration of 0.15 m indicates already the characteristic form of the absorption curve due to covalent molecules, when the concentration of $HClO_4$ is about 7 m. In either the same obtains even for a solution of 0.053 m of nitric acid, and in hexane the electrovalent form appears to be missing entirely.

We shall see below, that this specific influence of the outsi forces is in excellent agreement with the theory of the transiti from covalency to electrovalency.

Similar conditions obtain for other acids and their derivative The sulphate ion, even in supersaturated solutions at 40 C of ~~Mag~~ Na_2SO_4 does not show any selection absorption at all, but an end absorption only, just at the limit of the quartz spectrograph at about 225 m u. in solution of Na HSO_4 and $KHSO_4$ in strong concentration ~~and~~ in $Na.CH_3.SO_4$ in aqueous solutions a diffuse selectiv absorption has been found in the region between 300 and 250 m u and whose centre of gravity is difficult to determine. When both bonds become covalent i.e. in dimethyl sulphate and diethyl sulphate, a similar but more distinct selective absorption obtains, the maximum in the liquid state and in ether solutions lying at about 275 to 270 m u[11]. No experiments pertaining to the absorption of similar substance in the vapour state could be found in the available literature but since the Raman effect indicates a high percentage of covalent molecules $(H-O)_2SO_2$ in aqueous solutions containing about 50% of s sulphuric acid ($H_2SO_4 + 5H_2O$) ~~if~~ we decided to take the absorption of the esters in the liquid state and of H_2SO_4 in the vapour state as criterion of the covalent form. The bands of selective absorption in solution have been found rather later, because their absorption coefficient is 1000 to 5000 times smaller than in the case of the nitrates and necessitates to measure the absorption of the acid in the vapour state with long columns of the absorbing substance. With a tube of 80 cm. length and 2 mm vapour pressure I found selective

absorption in the vapour of pure H_2SO_4 in the region between and 260 m u with a maximum at about 262 m u resembling absorpt of the organic esters in contradistinction to the absorption o: the sulphate ion.

Aqueous solutions of KNO_2 have been measured by O. Halban ar Eisenbrand Eisenbrand[10] and possess a distinct absorption maximum at 375 m u. In the vapour state[12] the maximum is again shifted towards shorter wave length, i.e. to 363 m u in ethyl nitrite. This difference is, however, very small and it may well be that both maxima are identical, belong to a photodissociation common to the electrovalent and the covalent form, group, and that the maximum is shifted on account of polarisation in solution.

.....

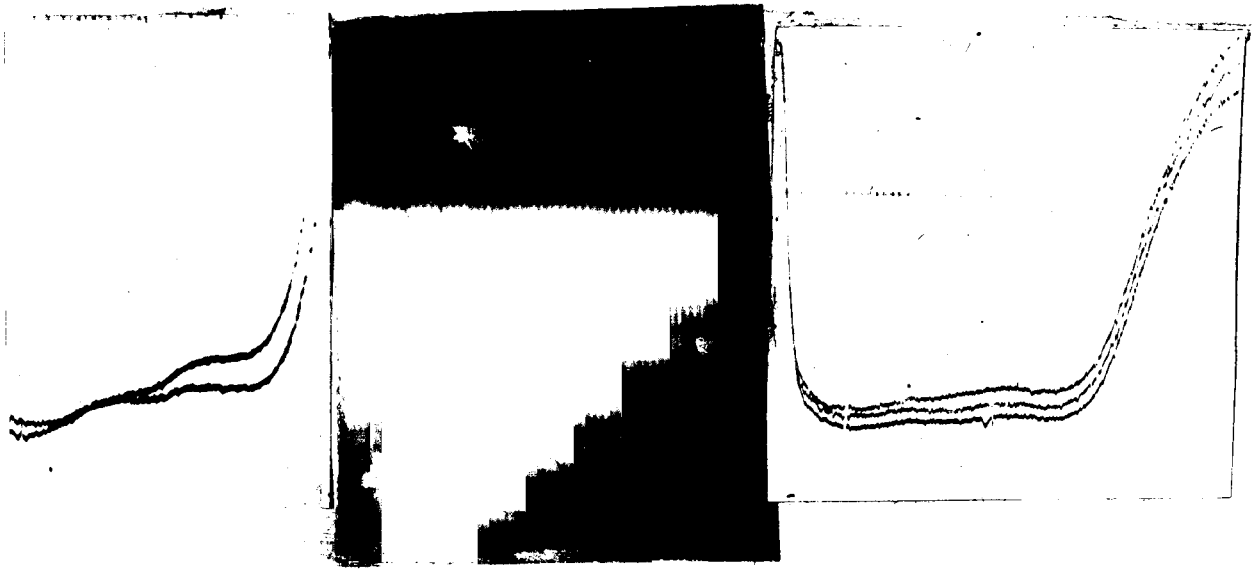
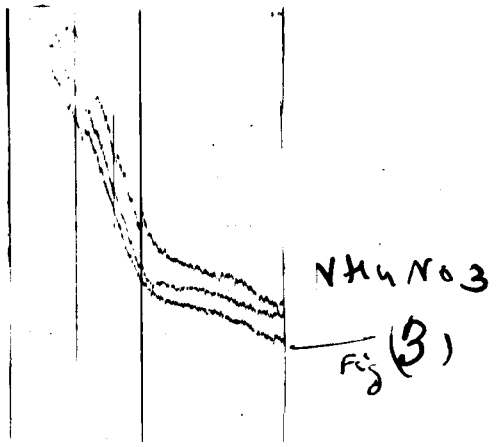


Fig (1) KNO_3

Fig (2) $AgNO_3$

Fig (4) $ZnSO_4$



NH_4NO_3

Fig (3)

E X P E R I M E N T A L.

The substances were heated in porcellaine tube of about 80 cm length in order to obtain clear absorption spectra even with low vapour pressures, i.e. at such low temperatures, where decomposition does not yet take place. The porcellaine tube was closed on both ends by heavy brass fittings carrying a quartz window each or which allowed a connection with the vacuum arrangement and were surrounded by cooling spirals. The continuous hydrogen spectrum was used as the source of light and a small Hilger quartz spectrograph as the resolving instrument. Besides the standard lines (Cu arc) an each plate absorption spectra through the empty tube and through the vapour in vacuum were taken with equal lines of exposure. Then plates were measured by means of a recording microphotometer (see figure 1 to 4) and the positon of the red wave limits and maxima determined directly on the photometer records.

After having placed the compounds in the absorption tube this was evacuated at room temperature for one to several hours, in order to remove the crystal water. This process was repeated for some hours at various temperatures in the range up to about 100° below the melting point of the anthydrous salt. Then the temperature was increased up to the melting point and above it, and the spectra taken.

The results are collected in table 1 and figures 1 to 4 are reproductions of the photometer records of KNO_3, $AgNO_3$, $(NH_4)NO_3$, and $ZnSO_4$. The spectra have been taken under the following conditions

Nitric acid, HNO_3. decomposes easily on heating.at 90° C the bands of NO_2 can be seen on the plate and with slightly higher temp.also

absorption bands of NO appear. The final plates have been taken after replacing the long porcellaine tube in this case by a small silic tube of 10 cm length varying the vapur pressure at room temperature. The selective absorption appears at 2 mm vapur pressure and is well developed at 4 mm.

(2) Potassium nitrate (M.P 336°C): The first of the two sets of NO_2 bands appear on the plates at the temperature of 475°. At 360 to 375° selective absorption obtains which disappears at higher temperatures along with the appearance of the NO_2 bands.

(3) Silver nitrate (M.P 208.5): Decomposition becomes rapid from 250° onwards, the selective absorption being well developed at 234° (see fig. 1.).

(4) Magnesium nitrate begins to decompose, according to the appearance of the NO bands already at about 170, the NO_2 bands appear at about 300°. The spectrum at lower temperatures (165°) shows rather an indistinct selective absorption which is better developed at 280 to 300°.

Cadmium nitrate (M.P. 350°) composes very rapidly. At 350° the two sets of NO_2 bands are already very strongly developed and fill almost the whole spectrum. The absorption spectrum of the vapour could not be obtained.

(5) Lead nitrate $Pb(NO_3)_2$. The No bands begin to appear at about 290°, those of NO_2 at 370°. The selective absorption of the vapour is present at 240° and is still better developed at higher temps.

(6) Ammonium Nitrate, NH_4NO_3. The decomposition of ammonium nitrate occurs first at about 200°C, indicated by the NO_2 bands, and becomes very rapid at about 280°C. The selective absorption is indicated at about 110°C and well developed at about 240°C.

(7) Sodium nitrite $NaNO_2$ (M.P.276.9). The decomposition is indicated by the appearance of the two NO_2 band systems, but it appears interesting that also the typical NO bands appear much stronger than in the nitrates. As a matter of fact, these latter bands begin to appear at about 275°, whereas the NO_2 bands are appreciably developed at 380° only. At both these temperatures the selective absorption of the salt in the vapour state is already unmistakably present on the photometer record.

(8) Sulphuric acid, H_2SO_4, is liable to rapid decomposition, when heated in the liquid state. The first SO_2 bands appear at about 110°C and they are fully developed at about 270°C and the decomposition appears to be almost complete at 400°C. The final plates were taken by placing the acid in a side bulb, and by selecting various vapour pressures without heating it. The selective absorption is well developed on plates, taken with a 80 cm tube and with 2 mm vapour pressure. It appears, however, as if some SO_2 still was present, because with increasing temperature and pressure not only the red wave limit but also the maximum shifts considerably towards longer waves, between the limits of 290 and 260 m u. We believe that the long wave maxima are produced by the superposition on the absorption, of un-resolved SO_2 bands and from a careful study of a greater number of plates and photometer records we think the value of 262 m u is the most probable one. Similar difficulties occured in K_2SO_4 and these two values are therefore less reliable than those of other compounds.

(9) Potassium sulphate $K_2(SO_4)$ (M.P.1067). The short wave SO_2 bands appear at 775°, the first of the near ultraviolet bands at 830°. The selective absorption of the salt is just indicated

at about 600° and very well developed at about 800°. Here similar ~~and~~ difficulties were encountered as in H_2SO_4, and the value of 254 m u appears to be the most probably one for the ~~maximum~~.

(10) Silver sulphate $Ag_2(SO_4)$ (M.P.660°). The first weak indications of the SO_2 bands appear already much below the melting point at about 180° and becomes the decomposition becomes rapid at about 300 to 350°. Selective absorption of the vapour obtains from 160° onwards.

(11) Zinc sulphate. Decomposition obtains from 550° onwards and becomes very rapid from 800° onwards.

(12) Ammonium sulphate is very resistable and decomposes easily, so much so that already near the melting point the near ultra-violet SO_2 bands cover the region of the probable selective absorption. ~~We~~ have not been ~~successful~~ to obtain a plate on which the selective absorption could be determined with complete certainty out some plates indicate that $(NH_4)_2SO_4$ behaves similar to K_2SO_4.

	Beginning of absorption. (M U)	Maximum. (M U)	Metransmission. (M U)	Remarks.
$(NO_3)^-$		302		Nitrates in dilute aqueous solution 11.12)
(HNO_3)		265		Nitric acid in hexane 11.12
$C_2H_5NO_3$		270		Ethyl nitrate in hexane[11.1]
$C_2H_5NO_3$		265		Vapour[13].
HNO_3	298	262	252	Vapour present paper 33547c
KNO_3	308	267	252	,, ,, ,, 32458c
$AgNO_3$	301	263	251	,, ,, ,, 33213
$Mg(NO_3)_2$	294	270	257	,, ,, ,, 349004
$Pb(NO_3)_2$	292	268	252	,, ,, ,, 34237
$NH_4 \cdot NO_3$	299	262	252	,, ,, ,, 33435
$(NO_2)^-$		375		HNO_2, dilute aqueous solution[11]
$C_2H_5NO_2$		363		Ethyl nitrite, vapur state[13]
$NaNO_2$	301	271	254	Vapour present paper (33213)
SO_4^-		225		Sulphates in dilute aqueous solution, max. probably in Schumann-region.
$(CH_3)_2SO_4$		275		Dimethyl sulphate, nomogen liquid
$(C_2H_5)_2SO_4$		270		Diethyl sulphate, nomog. liqu and sol. in ether.
H_2SO_4	235	262	261	Vapur, present paper 35078
K_2SO_4	293	258	254	,, ,, ,, 34120
As_2SO_4	300	265	250	,, ,, ,, 33237
$ZnSO_4$	294	269	242	,, ,, ,,

.....

The structure of Nitrates and Sulphates in the vapour state and the transition from Covalency to Electrovalency.

From table 1, where the results are summarised, it can be seen, that the figures are more or less the same for all the nitrates and all the sulphates respectively. Wether the individual differenees from salt to salt are genuine or not is difficult to say at the present moment. I has been pointed out in an earlier paper[3] that for continuous absorption spectra the positi of the red wave limit and, to a smaller degree, that of the maximum depends on temperature and vapour pressure, and these two factors vary very much in these experiments for the differe salts. For these salts the accurate determination of the wave lengths of the maxima becomes even more difficult, because the vapour pressure obtainable without decomposition, is rather low and the maximum themselves naturally rather flat and further experiments with even longer absorption cells and higher resolving power are necessary. It can be seen, however, that the absorption of the sulphates generally lies on the long wave side of the nitrates and that in both cases the region of selective absorption is close to that of the organic esters but very different from that of the free ions in solution. Hence, inorganic sulphates and nitrates are covalently bound in the vapour state. For the nitrites this is not yet certain, but probable.

This result is by no means surprising. The experiments of Franck and his collaborators[2] have shown that a transition from covalent to electrovalent linkage exists for the same molecule under different experimental conditions. Thus Ag Cl, well known to dissociate into Ag^+ and Cl^- ions in solution and in

the fused state possesses a covalent linkage in the vapour state according to its continuous absorption spectrum and its band spectrum in emission. Similarly HCl, HBr, HI are covalently bound in the vapour state according to their absorption spectrum their Raman effect and the value of their dipol moments[10]. There are only two possibilities, to explain these results. We have either to assume the existence of a particular class of molecules, which dissociate adiabatically into ions but are not made up of ions in their ground state, or, we assume that the bond may change from the covalent to the electrovalent character. In order to leave both ways open, Franck put forward the terminology of atomic binding and ionic binding, mentioned above. If the first explanation would be found valid, the terms electrovalent and covalent could be preserved with their chemical meaning and could denote compounds, which dissociate into ions or which do not respectively. If the second explanation holds, any bond would be either electrovalent or covalent at a particular moment, the two terminologies becoming identical, but the nature of the same bond would be found different under different conditions.

The influence of external conditions and forces on the nature of the bond may easily be seen from the Franck London diagram. Here the different effects of polarisation can be considered by introducing the changes of energy produced by them. Figure 5 contains the U: r curve of KCl. The ground state of this electrovalent molecule dissociates into $K^+ + Cl^-$. The level of the separated unexcited atoms K + Cl lies 0.6 volts (ionisation potential of K minus electronic affinity of Cl) below it and a flat repulsive curve originates from it, as can be seen from the red wave limit of its absorption spectrum in the vapour state.

The thermochemical energy of formation (K^+ Cl^-) K + Cl is 4.5 volts, the adiabatic dissociation energy (K^+ Cl^-) $K^+ + Cl^-$ is 5.1 volts. The energy of hydration is for the K^+ ion about 93 Kcal/mol, for the Cl^- ion about 89 Kcal/mol[13], together about 7 volts. The hydration energy of an undissociated electrovalent molecule (K^+ Cl^-) is of course not known, but it is clear, that the field outside such a molecule, in which the changes are counterbalanced, is much weaker, than that surrounding the separated ions. As a matter of fact, the dissociation of the molecule in solution proves, that the curve involving the separated hydrated ions (K^+ + a 9) + (Cl^- + a 9) is a repulsive one. The further question, whether a labile minimum position remains in the neighbourhood of the internuclear distance of the gaseous molecule (K^+ Cl^-) is of no interest here. It can be seen, however, that the level of the separated hydrated ions lies 1.9 volts below the ground level of the molecule.

Almost the same obtains for Ag Cl in spite of this molecule being covalently bound in its ground state. The ground level and the excited level possess a dissociation energy of 3.1 volts respectively[14]) according to its band spectrum the energy of excitation of the molecule being 3.9 volts. But the level of the separated ions lies in this case much higher, about 3.7 volts above that of the normal atoms, because the ionisation potential of Ag is much greater than that of K. In spite of this, the level of the hydrated ions becomes again the lowest one of the whole system, the hydration energy of Ag^+ being 100 Kcal/mol[13]) that of Ag^+ plus Cl^- being 8.2 volts. The level of (Ag^+ + aq) + (Cl^- + aq) therefore lies not only 4.5 volts below that of Ag + Cl but also 1.4 volts below the ground state of the

hence the repulsive curve involving the level of the separated ion interacts that of the ground state of the covalent molecule.

covalent garcous molecule. The actual position of the ionic curve is not known, but since the radius of Ag^+ is slightly smaller than that of K^+ and its polarisibility greater it will possess an adiabatic energy of dissociation of 5 to 6 volts, as indicated in the fig. The hydration energy of the covalent molecule will be much smaller and is entirely neglected here. These considerations make the mechanism of the transition from covalency to electrovalency perfectly clear. It occurs on account of the additional energies supplied by the interaction with surrounding molecules or ions in the liquid state the energies of solvation or hydration in solutions, the lattice energy in the crystal, and these will be big enough, when the minimum of the ionic curve is near to that of the covalent potential curve, which forms the ground-state of the molecule. This condition as can be seen from a comparison of figures 5 and 6, depends mainly on the position of the level of the separated ions with respect to that of the separated atoms. The changes in the adiabatic energies of dissociation are much smaller but those introduced particularly by the variation of the ionisation potential of the positive partner Therefore the difference, ionisation potential minus electronic affinity, determines roughly, whether such a transition from covalency to electrovalency is possible or not. Indeed, Samuel and Lorenz[16] could show, that a reat number of chemical phenomena as conductivities, hydrolysis, the character of an hydroxide as acid or base a.o, which are intimately connected with the transition from covalency to electrovalency, follow exactly this difference throughout the periodic system. It is of course possible to consider the reverse process, the transition from electrovalency to covalency (in a similar manner) e.g.

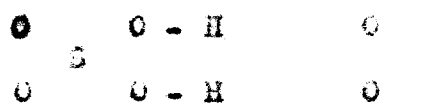
by the theory of deformation of Fajans. However, the above manner appears to be more satisfactory from a logical point of view and also to be a closer approach to reality. This can be seen from the fact, that in the sub-groups of the periodic system the transition from covalency to electrovalency always occurs easier of the molecules formed by the middle element e.g. Mg, Cd, In, than for those formed by both their neighbours Ca and Cu, Zn and Hg, Ga and Fe[17]. In a series like Cu, Cd, Hg, those properties, which form the parameter of transition in the theory of deformation like the ionic radius (0.83, 1.03, 1.12 Å U) and the polarisability of the ions (0.29, 2.44, 5.05) from a monotonous series, whereas the ionisation potential shows indeed a minimum for the middle element (first ionisation potentials = 9.4, 9.0, 10.4, second ones = 17.9, 16.8, 18.7 volts respectively for Cu, Cd, Hg).

The above considerations support the point of view taken up in this paper; such a transition is possible in the same molecule under different experimental conditions and therefore the terms of ionic and atomic binding and electrovalency and covalency respectively may well be identified. From the absorption spectra of diatomic halides Franck and his collaboratores had concluded, that those of H and Mg are covalently bound in the vapour state those alkali metals Na, K, Rb, and Cs indication electrovalent bond. Since H and Mg possess a high ionisation potential, the alkali metals a low one, it was expected a similar difference in the case of nitrates and sulphates, and, as far as the homogenous acids are concerned, covalency was already established by the Raman effect. This is supported by experiments of Butkow[17] which show, that triatomic halides are covalent in the vapour

state like those of Zn, Cd, and Hg, with high ionisation potential, but electrovalent, if the ionisation potential is low, as in those of Pb. But the experiments reported here show, that in this case even the alkali salts possess a covalent bond in the vapour state. This evidently is due to the electronic affinity of the nitrate and sulphate ion. Its exact value is not known, but it is clear, that it will be smaller in such a complicated system than for a simple halide ion. The above experiments indicate that the difference between the electronic affinity of the halides and these groups is considerable and greater than what could be expected.

As the absorption spectra in the vapour state indicate a covalent bond between the metal and the oxygen atom for the nitrates and sulphates, it appears, as if this phenomenon is rather common and we expect most of the simple inorganic salts (as distinct from genuine complex salts) to behave similarly. Further experiments on this point are in progress. In current literature the sulphate or nitrate ion is often described by a formula and NO_3^- indicating that such molecules belong salts. It has been pointed out[18] that according to spectroscopical results several classes have to be distinguished among the complex molecules, as the term is used today, and quite different mechanisms of linkage are responsible e.g for the existence of NO_3^-, $Cr(CN)_6^{3-}$ and $Cr(H_2O)_6^{3+}$ each of them representing a different type of chemical union. Werner himself was the first to assume that the sulphate and nitrate ion are really complex salts, but, while it can be understood that he tried to extend

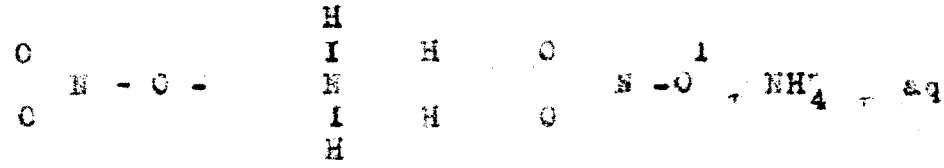
his new theory of co-ordination as far as possible, it should not be overlooked, that the arguments put forward by him do not hold any longer. As a matter of principle he did not want to make use of particular and definite ideas on the structure of atoms and did not want to ascribe different states of valency to the same atom. To day there is not the slightest difficulty to explain the tetra and hexa valency of sulphur on the basis of the configuration $s^2 p^4$ of the sulphur atom, the s electrons being active in the hexavalent but not in the tetravalent state. Again the experimental facts cited by Werner, do not warrant in themselves, the assumption of a co-ordinate bond for e.g. SO_4^{2-}. The hydrogen atoms are easily substituted in H_2SO_4, it is true, but this does not prove that they are bound in the second sphere of a complex because the same is true for the hydroxyl group too, as can be seen from the combination of H_2SO_4 and HCl to give SO_2Cl_2. Indeed just for such cases Werner ultimately had to assume a rearrangement into "ordinary valence compounds"[19]. To our mind the covalent bond in the vapour state indicates clearly that a discription by the older structural formulae.



are a close approach to reality, showing that such compounds can exist with the same number of valencies once in the covalent and once in the electrovalent state. Whether the two kinds of oxygen atoms, bound with a single and a double bond in the covalent form still can be distinguished in the free ion or not is a different question. Electronic configuration for both cases are conceivable

and a definite answer on this point cannot be given at this moment

Particular interest attaches itself to the spectrum of ammonium nitrate which does not form an exception but absorbs similarly to the other nitrates. Sidgwick[20] has introduced the "covalency maximum" of four for nitrogen on the basis of the Octet Theory and quotes the ammonium salts as examples, showing that the fifth bond of nitrogen cannot be covalent. Since $NH_4 \cdot NO_3$ in the vapour state absorbs like $C_2H_5\ NO_3$ and not like the free nitrate ion in solution, there appears to be no other possibility but to describe it by a formula



according to which nitrogen possesses 5 covalent bonds in the vapour state and the bond with highest polarisation becomes electrovalent on account of the external energies of the lattice or of hydration. As to the nitro-group, it has been proposed, to avoid the pentacovalency by the assumption of a resonance bond. For such a system, wave-mechanical calculation becomes rather complicated, but for a similar case, i.e. the $(HF_2)^-$ ion, quoted often along with the nitro group in this connection, it can be seen at once, that a resonance linkage does not exist. For this purpose we have to assume an ionic model for the ion, consisting of two F^- ions, bound together by a proton. This model corresponds exactly to that of H_2^+, made up of two H^+ ions, bound by a single electron, as it is used for wave-mechanical purposes only with the reverse signs. Therefore the results of the corresponding calculation[21] may be applied, and it can be seen, that the system $(FHF)^-$ indeed possesses a stable minimum position, like H_2^+ ; but because the proton is about 1840 times heavier than the electron,

the dissociation energy of HF_2^- would be 1840 times greater and the internuclear distance (F - F) 1840 times smaller than the corresponding dissociation energy and distance in H_2^+. If a physical meaning is at all attached to such a calculation, it cannot be anything else but that of an "united atom". At the internuclear distance of the $(HF_2)^-$ ion the system accordingly does not possess a stable minimum position, produced by wave-mechanical interaction.

On the other hand, the existence of this ion in solution is readily explained by electrostatic attraction between the dipole of non dissociated HF molecules and F^- ions and such an explanation makes it easily understood, why such phenomena are always confined to the elements with smallest atomic discussions, as has been pointed out elsewhere[22]. Also in this case ions like $(HCl_2)^-$ and $(HBr_2)^-$ do not exist. Resonance linkage is doubtless present in aromatic compounds, but because it accounts here for the particular aromatic properties, it is all the more probable a priori, that it does not exist in non-aromatic molecules, and it is therefore considered that the nitro group has to be conceived as derived from a pentacovalent nitrogen atom. As to the ammonium part of $NH_4 \cdot NO_3$ in the vapour state, there is little doubt, that nitrogen is pentacovalent according to the absorption spectrum and this agrees with recent indications of a pentacovalency of N in solutions of tetra-alkyl ammonium salts and certain evidence for the existence of NF_5[23].

The pentacovalency of nitrogen, indicated for a 2 ammonium nitrate is in the vapour state is also of interest, because Mulliken[24] uses the existence of the NH_4 ion with not more than 4 covalent linkages as a general argument, to interpret the method of molecular orbitals by means of the identification of

non-promoted and bonding electrons as a theory of valency in which the single electron possesses bonding power. The above results favour directly an electron pair bond theory of valency as suggested elsewhere [23].

Discussion of possible photodissociation Processes.

The correlation of the maxima observed in the vapour state and their red wave limit to particular processes of photodissociation meets with two difficulties. Firstly, as in all experiments concerned with continuous absorption spectra, it is difficult to determine the red wave limit belonging to the vibrationless molecule. As discussed elsewhere in some detail, the observed red wave limit will give too large values if the number of absorbing molecules is not sufficient to make the absorption complete, and it will give too small values, when a considerable percentage of the absorbing molecules is already excited to higher vibrational levels of the ground state, the number of collisions being increased by increased pressure or temperature. In this particular case the vapour pressure of the anhydrous salts is particularly small and we have tried to account for that

by an absorption tube of unusual length. The difference between the observed maxima and the red wave limit is about 300 A.U., and according to experience gained with other substances, such a figure should give a value not too much different from that of the vibrationless molecule. We believe, that the dissociation energies obtained from the beginning of the continuous absorption will be of the right order of magnitude and, if anything, rather too great than too small.

The second difficulty is the following: All inorganic nitrates in aqueous solutions of low concentration show the same selective absorption = 302 M U, which evidently has to be correlated to some process of photodissociation of the NO_3^- ions. Nitric acid in highly concentrated aqueous solutions, in non-dissociating solvents, organic nitrates in solution or measured as homogeneous substance, and all inorganic and organic nitrates in the vapour state exhibit the same selective absorption with its centre of gravity at about 265 to 270 M U; this evidently has to be correlated to some photodissociation of the covalently bound NO_3 group, since otherwise the above figure could not remain rather constant for so different partners as Na, H, and C_2H_5. Hence the transition from electrovalent to covalent linkage brings about a change in the dissociation process in such a way, that the dissociation energy is <u>increased</u>. In a similar way there exists some dissociation process for the sulphate ion with a red wave limit at 220 M U or below. Organic sulphates in the liquid state or solution, sulphuric acid and inorganic sulphates in the vapour state all possess a selective absorption = 270 to 290 M U. Similarly this has to be ascribed to a dissociation process concerning the covalently bound SO_4 group, and the

transition from electrovalency to covalency in this case brings about a change of the dissociation process which decreases the dissociation energy. But in both the groups, NO_3 and SO_4, in covalent linkage we have a central atom bound to oxygen atoms according to its maximal number of valencies and hence we should not expect dissociation processes, which are vastly dissimilar.

It could be possible to account for the above difference in behaviour, assuming that the spectra due to the negative nitrate and sulphate ions correspond to a dissociation process concerning not an atom but the superfluous electrons and are correlated to the electronic affinity of these ions. But then the electron affinity of e.g. SO_4 would be greater, not smaller than that of iodine. Moreover, Krishnan and Guha[25], have made it probable, that the two selective absorptions of the nitrate ions belong indeed to the two processes $NO_3^- \rightarrow NO_2^- + O(^3P)$ and $NO_3^- \rightarrow NO_2^- + O(^1D)$ Since they have taken the value of the red wave limit from absorption spectra in solution, the agreement between thermochemical determination and this value is not a definite proof, the beginning of the photodissociation of the free ions in the state of minimum vibration probably lies at higher energy values than they suppose, the potential curve of the repulsive state which is the final level of this transition, running rather step towards decreasing internuclear distance. That the red wave limit lies at higher values of the absorption coefficient than those selected by Krishanan and Guha, can be seen from a comparison of the absorption spectra of many compounds in the vapour state and in solution, but nevertheless, the above correlation is made quite plausible, because the energy difference between the two maxima of NO_3^-, i.e. 302 and 193 M U is about 2.3 volts in fair

agreement with the excitation energy 1.9 volts of O (^1D),and the energy difference of the maxima is always, more reliable than that of the red wave limits. They calculate for the dissociation process $NO_3^- \rightarrow NO_2^- + O(^3P)$ the energy difference of about 83 Kcal/mol in dilute aqueous solution.

As to the absorption spectra of the covalent molecules, it is by no means possible definitely to decide on the photodissociation connected with them. The known energies of formation of acids and salts cannot be used to calculate the atomic heat of formation, because they all refer to measurements in the crystalline state or in solution, in which these corresponds possess an electrovalent bond. Furthermore, it is not possible to calculate the atomic energy of formation from these values by means of some cycle, because a number of the necessary quantities, e.g. the electron affinity of NO_3 are not known.

Atomic energies of formation of similar covalent molecules are however, available for organic eshers of nitrons and nitric acids i.e. for ethyl nitrate and ethyl nitrate, which can be calculated from the known heats of combustion. There are for the gaseous molecules 324 and 334 Kcal/mol respectively. When calculating the atomic energies of formation and deducting one from the other, again all quantities cancel out with the exception of 1/2 D (O_2) and hence the dissociation process $C_2H_5 \cdot O \cdot NO_2 \rightarrow C_2H_5 \cdot O \cdot NO + O$ respresents an energy of 10 + 59 = 69 Kcal/mol. The same value obtains for the anhydrideof nitric and nitroges acid. The energies of formation from the elements are $\lambda(N_2O_5) = 1.2$, and $\lambda(N_2O_3) = 22$ Kcal/mol and gives the atomic energies of formation D (N_2O_5) = 463 and D (N_2O_3) = 325 Kcal/mol or 69 Kcal/mol for the dissocia-

tion process $1/2\ N_2O_5 \longrightarrow 1/2\ N_2O_3 + O$

The dissociation process $SO_4^- \longrightarrow SO_3^- + O(^3P)$ may be considered in a similar way. The following figures are obtained by adding half of the dissociation energy of O_2 to the heat of formation $\zeta(M_2SO_4)$ of the sulphates from the elements in aqueous solutions and deducting the corresponding heat of formation of the sulphites $\zeta(M_2SO_3)$:

M =	Na	K	NH_4	g*)
$\zeta(M_2SO_4)$	328	334	280	302
$+ 1/2\ D(O_2)$	59	59	59	59
$- \zeta(M_2SO_3)$	264	275	214	240
$SO_4^- \longrightarrow SO_3^-$	123	118	125	121

The atomic heat of formation of SO_2 has been calculated to 247, that of H_2O to 217 Kcal/mol,. The heat of solution of $SO_2 + aq$ is about 6 Kcal/mol, and the atomic heat of formation of H_2SO_3 in dilute aqueous solutions comes to about 470 Kcal/mol of sulphuric acid in dilute aqueous solution gives an atomic energy of formation of 607 Kcal/mol, and the dissociation energy of the process $H_2SO_4 + aq \longrightarrow H_2SO_3 + aq + O$ is about 137 Kcal/mol. This value is slightly higher than that obtained from the salts, and the difference may be due to different degrees of dilution. It is, however, not impossible, that sulphuric acid behaves slightly different from the sulphates, because also in the vapour state

*) These figures refer to the solid state.

the spectrum of the acid is slightly shifted against that of the salts. For the splitting off of a neutral oxygen atom from the free SO_4^{2-} ion we may take an energy value of roughly 125 Kcal/mol This corresponds to a wave length of 227 M U. The absorption of the sulphate ion indeed begins in this region and appears to be correlated to this process.

For covalent molecules of this type the corresponding energies cannot be calculated, because energies of combustion of organic eshers of sulphuric and sulphurous acid are not known. For the anhydrides of the acids from the values $\frac{1}{2}(SO_3) = 92$ and $\frac{1}{2}(SO_3) = 71$ Kcal/mol by the addition of $1/2\ D(O_2)$ a value of 80 Kcal/mol is obtained for the splitting off of an oxygen atom in the gaseous be taken as valid for the organic esners provisionally. In analogy to ethyl nitrate and ethyl nitrite this value may state.

In other words, the energy of this dissociation process is reduced from 125 Kcal/mol for the hydrated ion to 80 Kcal/mol for the gaseous covalent molecule. While the first value agrees with the beginning of the absorption spectrum in aqueous solution, the latter one corresponds closely to the red wave limit of sulphates and sulphuric acid in the vapour state. The meanxmfix of the above observations is about 90 Kcal/mol is not significient in any way, because, firstly, the vapour pressure naturally was very small and, secondly, the upper repulsion potential curve runs parallel to the abscissa of the internuclear distance of the U : r diagram only in rare cases. The above figures explain why the absorption is snifted towards longer wave length in the transition from electrovalency to covalency and it appears, as if the beginning of the absorption was to be correlated to the dissociation of an unexcited O atom in both cases.

For the nitrates, however, the difficulty which was mentioned above remains i.e. that the absorption is shifted to shorter wavelength by the same transition from electrovalency to covalency contrary to the behaviour of the sulphates, while the energy of the dissociation process is decreased from 83 to 69 Kcal/mol respectively, in a similar manner, as either case of the sulphates. This may be explained, of course, by a different slope of the repulsive curve. We know indeed a large number of polyatomic molecules, e.g. the type CH_3 Cl, where the energy of dissociation, re-assured optically is much too large on account of the steepness of the upper potential curve. it should be borne in mind, that the energy differences measured by the red wave limit of the continuous absorption spectrum in reality are energies of electronic excitation of the molecule, which depend on the potential curve not only of the ground state but of the final state as well. But still, this disagreement is by no means satisfactory, particularly considering the good agreement obtained for sulphates, and since various other photodissociation processes are possible, a definite correlation of the red wave limit of the absorption in the gaseous state may be reserved for a time, till more experimental data of other inorganic salts are available.

Again the second red wave limit, i.e. the point of retransmission, cannot be explained satisfactorily at present. The energy difference between the first and second red wave limit is about 0.8 volts for the nitrates and about 1 volt for the sulphates, & these values do not agree either with the term difference $^1D - ^3P$ of oxygen or with its triplet separation. The difference between the absorption maxima which is not yet known, would give clearer results and also the discussion on this question has to postponed.

References.

1 A preliminary account of the following paper has already been published in "Nature".

2 Cf. J. Franck: Trans. Faraday Soc. 21,526, 1925.

Cf. R. Samuel: " Absorption Spectra etc.,.

Cf. L.A. Woodward: Annual Rep. Chem.Soc.Vol.31,1935.

3 P.K.Sen Gupta: Bull. Ac. Sci (Allahabad) 3, 203, 1934.

4 H. Leasheim and R.Samuel: Z.Phys.84, 637, 1933, 88, 276, 1934. Proc. Ind. Ac.Sci. (Bangalore) 1, 623, 1935. Phil. Mag. 21, 41, 1936. B.C.Mahanti: Ind.J.Phys. 9, 517, 1935. Cf.R.Samuel, "Absorption Spectra etc., (ref.2).

5 R.K. Asundi, R.Samuel and Mohd. Zaki-Uddin: Proc.Phys.Soc. (London) 47, 235, 1935.

6 Cf. R.Samuel, "Absorption Spectra etc.

7 -do- -do- -do- -do-

8 -do- -do- -do- -do-

9 -do- -do- -do- -do-

10 -do- -do- -do- -do-

12 J.Wallace Goodeve: Trans. Farad. Soc. 30, 504,1934.

11 L.Lorenz and R.Samuel: Z.Phys. Chem. (B) 14, 219, 1931 S. Mujtaba Karim and R.Samuel: Proc. Ind.Ac.(Bangalore) 1, 398, 1934.

R.Samuel " Absorption Spectra etc. " (ref.2.) and Curr.Sci. 3, 549, 1935.

13 Taken from the article of H.G.Grimm and L.Wolff, Handb. D. Phys. 24, Berlin 1933. p. 1051.

3. R. K. Asundi and R. Samuel : Pro. Phy. Soc. London 48, 28, 193,

16 R.Samuel and L.Lorenz: Z. Phys. 59, 53, 1929.

17 Cf. R.Samuel and L.Lorenz (22), H.Lesaheim and R.Samuel (19) E. Butknow: Z. Phys. Chem (B) 12, 369, 1931; Phys. Z. (Sowjetunion) 4, 577, 1933.

18 R.Samuel: "Absorption Spectra etc." ref.(2).

20 N.V.Sidgwick: "Electr. Theory of Valency" (Oxford 1927); contribution to the "Annual Reports Chem. Soc.", perticularly 1935.

22 T.F.Hunter and R.Samuel: J.C.S. 1934, 1180, Chem. and Ind. 54, 31, 467, 635, 1935.
L.Staub: Dissertation, Breslau.

25 K.S.Krishnan and A.C.Guha: Proc. Ind. Ac. Sci. (Bangalore) 1, 242, 1934. cf. D.K. Narayanswami: Trans.Faraday Soc. 31, 1411, 1935.

21 E. Teller, Z. Phy. 61, 458, 1930

23. Cf. sh. Nawazish Ali and R. Samuel in the Journal —